⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　昭60－192333

⑤Int.Cl.⁴　識別記号　庁内整理番号　㊸公開　昭和60年（1985）9月30日
H 01 L 21/30　Z－6603－5F
G 03 F 7/00　101　7124－2H
審査請求　未請求　発明の数　1　（全4頁）

㉔発明の名称　有機塗布硬化膜の除去方法

㉑特　願　昭59－47653
㉒出　願　昭59(1984)3月13日

㉗発明者　松崎　晴美　日立市幸町3丁目1番1号　株式会社日立製作所日立研究所内
㉗発明者　高橋　燦吉　日立市幸町3丁目1番1号　株式会社日立製作所日立研究所内
㉗発明者　吉田　正博　日立市幸町3丁目1番1号　株式会社日立製作所日立工場内
㉗発明者　高草木　常彦　日立市幸町3丁目1番1号　株式会社日立製作所日立工場内
㉑出願人　株式会社日立製作所　東京都千代田区神田駿河台4丁目6番地
㉔代理人　弁理士　鵜沼　辰之　外1名

最終頁に続く

明　細　書

発明の名称　有機塗布硬化膜の除去方法

特許請求の範囲

1. 有機塗布硬化膜が接合された基板から有機塗布硬化膜を除去する方法において、前記有機塗布硬化膜が接合された基板と液化ガス又は超臨界ガスとを接触させた後、該ガスの温度および／又は圧力の条件を変えて前記ガスを膨張させることを特徴とする有機塗布硬化膜の除去方法。

2. 前記ガスが有機溶剤を含有することを特徴とする特許請求の範囲第1項記載の有機塗布硬化膜の除去方法。

3. 前記基板が半導体ウエハであり、前記有機塗布硬化膜が、ホトレジスト材からなることを特徴とする特許請求の範囲第1項記載の有機塗布硬化膜の除去方法。

4. 前記半導体ウエハは、Si単結晶板にSiO_2，SiN又はAℓ等の保護膜が形成され、ホトレジスト材および保護膜はパターンエッチングが終了されたものであることを特徴とする特許請求の範囲第3項記載の有機塗布硬化膜の除去方法。

5. 前記ホトレジスト材が、ネガ又はポジタイプであることを特徴とする特許請求の範囲第3項又は第4項記載の有機塗布硬化膜の除去方法。

発明の詳細な説明

〔発明の利用分野〕

本発明は有機塗布硬化膜が接合された基板から有機塗布硬化膜を除去する方法に係り、特に半導体ウエハのホトレジスト塗布膜の塗布膜を剝離するのに好適な方法に関する。

〔発明の背景〕

半導体ウエハはSi単結晶板にSiO_2，SiN又はアルミ等の保護膜が形成された後、これらの保護膜の面にホトレジスト材を塗布し、所定のパターンで露光によつて所定のパターンに重合させ次いでパターンエッチングによつて所定のパターンのホトレジスト塗布膜と保護膜を形成し、次いで不純物をドーピングする操作が行なわれている。このようなパターンエッチングが終了した半導体ウエハではホトレジスト塗布膜を除去する必要がある。従来このようなホトレジ

スト塗布膜の除去方法として、熱硫酸，硫酸あるいは過酸化水素のような強力な酸化剤でホトレジスト塗布膜を溶解する方法が行なわれている。しかしこのような強力な酸化剤を用いる方法では、処理剤中にホトレジスト膜成分が溶解するために処理液の再使用が困難であり処理液の寿命が短いという欠点がある。また処理の仕方によつてはホトレジスト膜の下地材料を侵す恐れもある。一方ホトレジスト膜の下地材料の耐薬品性を考慮してフエノール系有機材料、ハロゲン系有機溶剤などの特別な剝離剤でホトレジスト塗布膜を剝離する方法も行なわれている。しかしこれらの有機溶剤を用いる方法では溶剤の後処理が環境保全上必要であり、引火性薬品のため取り扱い上の問題も生じる。更に低温酸素プラズマによる灰化方法も行なわれているが、この方法ではホトレジスト膜中に含有される重金属は除去できないためホトレジスト膜を除去した後もこれらの重金属は半導体ウエハ面に残存するため新たに重金属を除去する処理が必要となる。

このように従来のホトレジスト塗布膜の除去方法で生じる問題点は、処理液の異常拡散による素子特性の劣化、不純物によるSiO_2の汚染と素子特性の不安定化、絶縁耐圧の劣化などによる素子の歩留まりを低下させているのが現状である。

〔発明の目的〕

本発明は、不純物によるSiO_2などの保護膜の汚染や素子特性の劣化を防止し、素子の歩留まりの低下を防止できるとともに処理液の再使用が容易な有機塗布硬化膜の除去方法を提供することにある。

〔発明の概要〕

本発明はホトレジスト塗布膜のような有機塗布硬化膜を溶解、化学的剝離、酸化などの現象を利用することなく物理的に剝離する方法を提供するものであつて、有機塗布硬化膜が接合された基板から有機塗布硬化膜を除去する方法において、前記有機塗布硬化膜が接合された基板と液化ガスは超臨界ガスとを接触させた後、該ガスの温度及び／又は圧力の条件を変えて前記ガスを膨張させ、

この膨張力によつて基板から有機塗布硬化膜を除去するようにしたものである。

本発明において、有機塗布硬化膜が接合された基板を高圧下で液化ガスは超臨界ガスと接触させ有機塗布硬化膜自体にあるいは有機塗布硬化膜と基板との界面部に液化ガス又は超臨界ガスを溶解させ、液化ガス超臨界ガスの圧力を低減するか又は液化ガス又は超臨界ガスの温度を上昇させる。これによつて有機塗布硬化膜内あるいは有機塗布硬化膜と基板との界面部に存在する溶解液化ガス又は溶解超臨界ガスが膨張し、この膨張力によつて基板から有機塗布硬化膜が剝離される。液化ガス又は超臨界ガスの溶剤としての特性を利用した液化ガス抽出法や超臨界ガス抽出法は種々提案されている。これらの方法では（Ａ）溶解力が大きいこと、（Ｂ）選択性を有すること、（Ｃ）抽出物と溶剤との分離が容易であることなどの溶媒としての特性が利用されている。

本発明は（Ａ）溶剤ガスの溶解性と（Ｂ）減圧又は昇温による液化ガス又は超臨界ガスの膨張力

を利用するものであつて、従来の抽出法とは原理も目的も異なる。

ここで、超臨界ガスとは、圧力－温度の状態図において、臨界温度以上、かつ、臨界圧力以上の状態にあるものを言う。液化ガスとは、圧力－温度の状態図において、飽和蒸気圧線以上の圧力状態にあり、大気圧下で通常の温度においてはガス状であるものを言う。

本発明において液化ガス又は超臨界ガスとしてはCO_2，NH_3，N_2などの非酸化性ガスが使用できるが、コストおよび操作面でCO_2が好適である。また常温でガス状の有機溶剤は単独でも使用できる。このような有機溶剤としてプロパン，ブタン，塩化メチル、などを用いることができる。これらのガス状有機溶剤は高圧及び低温にすることによつて液化ガス又は超臨界ガスとすることができる。液化炭酸ガスの場合、ホトレジスト塗布膜のような有機塗布硬化膜などの内部又はこれらの膜と基板との界面に完全に侵透しにくいので、この場合炭酸ガスに溶解性の高い有機溶媒を混合すること

が望ましい。有機溶媒の混合によつて液化ガスの急激な減圧を行なう場合、急激な減圧時の衝撃を緩和する役目を果たす。液化炭酸ガスと相互溶解性の高い有機溶媒としては、炭化水素系、ハロゲン化炭化水素系、アルコール系、ケトン系などの有機溶媒があげられる。炭化水素系有機溶媒、例えば、ヘキサン、石油エーテル、ベンゼン、トルエンなどの有機溶媒は液化炭酸ガスに完全に溶解する。またハロゲン化炭化水素系有機溶媒、例えばジクロルメタン、フロンなどは静止状態では不溶であるが攪拌すれば溶解する。アルコール系有機溶媒、例えばエタノール（無水）は液化炭酸ガスに完全に溶解するが、エタノール（含水）は液化炭酸ガスに一部溶解する。またケトン系有機溶媒、例えばアセトンは液化炭酸ガスに完全に溶解する。従つて液化炭酸ガスに混合する有機溶媒は有機塗布硬化膜に対する溶解性あるいは基体を損傷しない特性などを総合的に考慮して選択すべきである。超臨界ガスの場合にも塗布硬化膜に対する溶解及び有機塗布硬化膜と基板との界面に対する侵透性をより完全なものにするためには超臨界ガスに有機溶媒を混合することが望ましい。

有機溶媒を用いる場合、少量の有機溶媒中に多量の溶剤ガスが溶解するため使用する有機溶剤量は少なくてすむ。第1図は液化炭酸ガス（以下L－CO_2と略す）とエチルアルコール水溶液との総合溶解性を示す実験データである。横軸は温度、縦軸はエチルアルコール水溶液中に溶解するL－CO_2量及びL－CO_2中に溶解するエチルアルコール水溶液量であつて、エチルアルコール水溶液のアルコール濃度がパラメータである。第1図から温度16℃一定とし、横軸にエチルアルコールのアルコール濃度をとると第2図のように示され、濃度が90vol%以上では相当量のL－CO_2がエチルアルコール水溶液中に溶解することがわかる。

〔発明の実施例〕

実施例により本発明を詳細に説明する。

実施例1

ホトレジスト塗布膜の厚さが約10μのパターンエッチングが終了した電力用のウエハとL－CO_2を室温下で所定時間、ベッセル内で接触させた後、ベッセル内圧力を大気迄急激に減圧した。ホトレジスト塗布膜は基板からきれいに剝離脱落した。

実施例2

ホトレジスト塗布膜厚さが約10μのパターンエッチングが終了した電力用のウエハと圧力75atg、温度35℃の超臨界炭酸ガスとをベッセル内で接触させ、ベッセル内圧力を大気圧まで急激に減圧した。この際ガスの吸引方向を半導体ウエハの平面部と平行する方向に行なつた。その結果ホトレジスト塗布膜は基板からきれいに剝離脱落しウエハの破損はなかつた。

実施例3

ホトレジスト塗布膜厚さが約10μのパターンエッチングが終了した電力用のウエハとL－CO_2およびエチルアルコールとの混合溶剤とを室温下でベッセル内で接触させ、ベッセル内圧力を大気圧まで急激に減圧した。その結果ホトレジスト塗布膜は基板からきれいに剝離脱落した。なおガスの吸引方向は実施例1と同様であり、ウエハの破損はなかつた。本実施例においてはL－CO_2中のエチルアルコールの存在によつて減圧時の衝撃は緩和されたため、ウエハの破損は生じなかつたものと思われる。

〔発明の効果〕

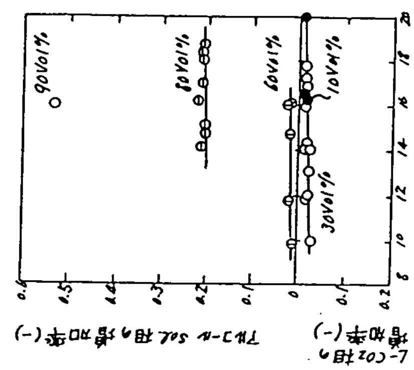
以上のように本発明によれば、基板に接合された有機塗布硬化膜を物理的に剝離除去するため、薬品による酸化分解、溶解等によつて生じる素子特性の劣化がないため素子の歩留まり向上につながる。またホトレジスト塗布膜のように酸化物薄膜からなる保護膜を設ける場合には不純物によるSiO_2の汚染と素子特性の不安定化、絶縁耐圧の劣化がなく更に次工程における酸化膜除去洗浄が不要となる。また剝離除去されたホトレジスト塗布膜のような有機塗布硬化膜は処理液中に固形物として存在するため回収が容易であり、このため排液処理は大幅に簡略化される。

図面の簡単な説明

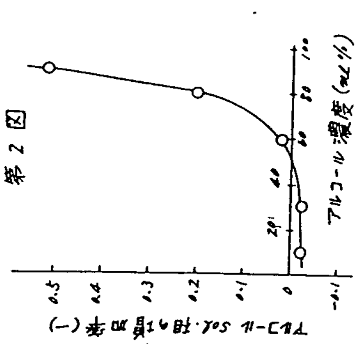
第1図及び第2図は液化炭酸ガスとエチルアルコール水溶液との総合溶解性を示すグラフである。

代理人　弁理士　山口　巖

第1図



第2図



第1頁の続き
⑫発 明 者　佐 藤　譲 之 良　日立市幸町3丁目1番1号　株式会社日立製作所日立工場内
⑫発 明 者　八 木　秀 幸　日立市幸町3丁目1番1号　株式会社日立製作所日立工場内

(11) Japanese Patent Publication No. JP-A-60-192333

(43) Date of Publication: September 30, 1985

(21) Application Number: 47653/1984

(22) Date of Filing: March 13, 1984

(71) Applicant: Hitachi, Ltd.

(72) Inventors: Harumi MATSUZAKI

Sankichi TAKAHASHI

Masahiro YOSHIDA

Tsunehiko TAKAKUSAKI

(74) Agent: Tatsuyuki UNUMA, patent attorney (One other)

SPECIFICATION

Title of the Invention

METHOD OF REMOVAL OF ORGANIC COATED AND HARDENED FILM

[Claim for Patent]

1. A method of the removal of an organic coated and hardened film from a substrate with which the organic coated and hardened film is joined, the method comprising bringing the substrate, with which said organic coated and hardened film is joined, into contact with liquefied gas or supercritical gas and thereafter expanding said gas by changing the temperature and/or pressure conditions of the gas.

2. A method of the removal of an organic coated and hardened film according to Claim 1, wherein said gas contains an organic solvent.

3. A method of the removal of an organic coated and hardened film according to Claim 1, wherein said substrate is a semiconductor wafer and said organic coated and hardened film comprises a photoresist material.

4. A method of the removal of an organic coated and hardened film according to Claim 3, wherein said semiconductor wafer comprises a Si monocrystal plate on which a protective film such as SiO_2, SiN or Al is formed and the photoresist material and the protective film are those of which a pattern etching has been finished.

5. A method of removal of an organic coated and hardened film according to Claim 3 or Claim 4, wherein said photoresist is a negative or positive type.

Detailed Description of the Invention

[Field of Application of the Invention]

The present invention relates to a method of removing an organic coated and hardened film from a substrate with which the organic coated and hardened film is joined, and, particularly, to a method suitable to peel off a coated film of a photoresist coated film of a semiconductor wafer.

[Background of the Invention]

With regard to a semiconductor wafer, the following operations are carried out: a protect layer such as SiO_2, SiN or aluminum is formed on a Si monocrystal plate, a photoresist material is then applied to the surface of these protective films, the photoresist material is polymerized into a predetermined pattern by exposure to a prescribed pattern, a photoresist coating film and protective film having a prescribed pattern are formed by a pattern etching and thereafter the substrate is doped with impurities. It is necessary to remove the photoresist coated film from such a semiconductor wafer of which a pattern etching is finished. As a conventional method of removing such a photoresist coated film, a method in which a strong oxidant such as hot sulfuric acid, sulfuric acid or hydrogen peroxide is used to solve the photoresist coated film. However, the method using such a strong oxidant has the drawback that the reuse of a process solution is difficult and the life of the process solution is short since a photoresist film component is dissolved in the process agent. Also, a base material under the photoresist film is possibly eroded depending on the way of the treatment. While a

method is used in which a photoresist coated film is peeled off using a special peeling agent such as a phenol type organic material or halogen type organic solvent in consideration of the chemical resistance of the base material under the photoresist film. In the method using these organic solvents, however, post-treatment of a solvent is required in view of environmental safeguard and a handling problem arises because these solvents are flammable chemicals. Moreover, an ashing method using a low temperature plasma is carried out. In this method, however, because heavy metals contained in a photoresist film cannot be removed, these heavy metals remain unremoved on a semiconductor wafer even after the photoresist film has been removed, which requires additional treatment for removing the heavy metals.

As stated above, these problems which arise in the conventional methods of removing a photoresist coated film cause a deterioration of elemental properties on account of irregular diffusion of a process solution, the contamination of SiO_2 and unstabilization of elemental properties caused by impurities and reduced yield of elements on account of deteriorated dielectric voltage resistance at present.

[Object of the Invention]

The present invention is to provide a method of the removal of an organic coated and hardened film, the method preventing the contamination of a protective film, e.g., SiO_2 and deterioration in the characteristics of elements caused by impurities, avoiding a reduction in yield of elements and enabling easy reuse of a process solution.

[Summary of the Invention]

The present invention is to provide a method of peeling off an organic coated and hardened film such as a photoresist coated film physically without making use of a phenomenon such as dissolution, chemical peeling or oxidation and resides in a method of the removal of an organic coated and hardened film from a substrate with which the organic coated and hardened film is joined, the method comprising bringing the substrate, with which said organic coated and hardened film is joined, into contact with liquefied gas or supercritical gas and thereafter expanding said gas by changing the temperature and/or pressure conditions of the gas, thereby removing the organic coated and hardened film by the expansion force.

In the present invention, a substrate with which an organic coated and hardened film is joined is brought into contact with liquefied gas or supercritical gas under pressure to dissolve the liquefied gas or the supercritical gas either in the organic coated and hardened film itself or in the boundary between the organic coated and hardened film and the substrate, thereby decreasing the pressure of the liquefied gas, supercritical gas or lowering the temperature of the liquefied gas or supercritical gas. The dissolved liquefied gas or supercritical gas existing in the organic coated and hardened film or in the boundary between the organic coated and hardened film and the substrate is expanded and the organic coated and hardened film is peeled from the substrate by the expansion force. A variety of liquefied gas extraction methods and supercritical gas extraction methods utilizing the properties of liquefied gas or supercritical gas as a solvent have been

proposed. In these methods, the properties as a solvent such as (A) large solubility, (B) high selectivity and (C) easy separability of the extract from a solvent are utilized.

The present invention utilizes (A) the solubility of solvent gas and (B) the expansion force of liquefied or supercritical gas which force is obtained by pressure reduction or a rise in temperature and is hence different from the conventional extraction methods in principle and object.

Here, the supercritical gas means those which are in the condition of more than supercritical temperature and supercritical pressure in the pressure-temperature constitutional diagram. The liquefied gas means those which are in a pressure condition above the saturated vapor pressure line in the pressure-temperature constitutional diagram and have a gaseous form at normal temperature under atmospheric pressure.

In the present invention, non-oxidizing gas such as CO_2, NH_3 or N_2 may be used as the liquefied gas or the supercritical gas. CO_2 is desirable in view of costs and operations. Also, organic solvents having a gaseous form at normal temperature may be used even singly. As such a solvent, propane, butane, methyl chloride or the like may be used. These gaseous organic solvents may be changed to liquefied gas or supercritical gas under increased pressure or at lowered temperature. In the case of liquefied carbon dioxide gas, it can perfectly penetrate with difficulty into the inside of an organic coated and hardened film such as a photoresist coated film or into the boundary between each of

these films and a substrate. In this case, therefore, it is desirable to mix a highly soluble organic solvent in carbon dioxide gas. When a sudden reduction in the pressure of liquefied gas is made by the mixing of an organic solvent, the solvent serves to lighten the impact produced when the pressure is suddenly reduced. Given as examples of organic solvent having high mutual solubility with liquefied carbon dioxide are hydrocarbon type, hydrocarbon halide type, alcohol type and ketone type organic solvents. Hydrocarbon type organic solvents such as hexane, petroleum ether, benzene and toluene completely solve in liquefied carbon dioxide gas. Also, though hydrocarbon halide organic solvents such as dichloromethane and Freon are insoluble in a static state but become soluble by stirring. As for alcohol type organic solvents, for example, ethanol (anhydride) thoroughly dissolves in liquefied carbon dioxide gas and ethanol (hydrate) partially dissolves in liquefied carbon dioxide gas. Also, ketone type organic solvents, for example, acetone thoroughly dissolves in liquefied carbon dioxide gas. Therefore, the organic solvent to be mixed in liquefied carbon dioxide gas must be selected in overall consideration of, for instance, the solubility in the organic coated and hardened film and the characteristics decreasing damages to the substrate.

In the case of supercritical gas, it is desirable to mix an organic solvent in the supercritical gas to provide the gas with more perfect solubility in the coated and hardened film and with more perfect penetrability into the boundary between the organic coated and hardened film and the substrate.

In the case of using an organic solvent, only a small amount of the organic solvent suffices the requirements since a large amount of solvent gas dissolves in a small amount of the organic solvent. FIG. 1 is experimental data showing the total solubility of liquefied carbon dioxide gas (hereinafter abbreviated as L-CO_2) in an aqueous ethyl alcohol solution. The abscissa shows temperature and the ordinate shows the amount of L-CO_2 dissolved in an aqueous ethyl alcohol solution and the amount of an aqueous ethyl alcohol solution dissolved in L-CO_2, wherein the concentration of alcohol in the aqueous ethyl alcohol solution is a parameter. Fig. 2 is resulted from FIG. 1 when the temperature is fixed at 16°C and the concentration of alcohol in an aqueous ethyl alcohol solution is taken as a function of the ordinate in FIG. 1. It is found that when the concentration is 90 vol% or more, a considerable amount of L-CO_2 dissolves in an aqueous ethyl alcohol solution.

[Examples of the Invention]

The present invention will be explained in more detail by way of examples.

Example 1

A power wafer provided with about a 10-μm-thick photoresist coated film of which a pattern etching had been finished was brought into contact with L-CO_2 at ambient temperature for a predetermined time in a vessel. Then the pressure in the vessel was dropped rapidly to atmospheric pressure. The photoresist coated film was thoroughly peeled and falls away from the substrate.

Example 2

A power wafer provided with about a 10-μm-thick photoresist coated film of which a pattern etching had been finished was brought into contact with supercritical carbon dioxide gas having a pressure of 75 atg and a temperature of 35°C in a vessel. Then the pressure in the vessel was dropped rapidly to atmospheric pressure. At this time, the direction in which gas is sucked was set to a direction parallel to the plane portion of the semiconductor wafer. As a consequence, the photoresist coated film was thoroughly peeled and falls away from the substrate without the breaking of the wafer.

Example 3

A power wafer provided with about a 10-μm-thick photoresist coated film of which a pattern etching had been finished was brought into contact with a mixture solvent consisting of L-CO_2 and ethyl alcohol at ambient temperature in a vessel. Then the pressure in the vessel was dropped rapidly to atmospheric pressure. As a consequence, the photoresist coated film was thoroughly peeled and falls away from the substrate. Further, gas was sucked in the same direction as in Example 1 and no breaking of the wafer was found. It is thought that no breaking of the wafer was caused because the existence of ethyl alcohol lightened the impact when the pressure was dropped.

[Effect of the Invention]

As stated above, according to the present invention, an organic coated and hardened film joined with a substrate is physically peeled and removed and hence there is no deterioration in the characteristics

of elements which deterioration is caused by oxidation decomposition and dissolution by chemicals, leading to an improvement in the yield of elements. Also, when a protective film, such as a photoresist coated film, consisting of a thin oxide film, the contamination of SiO_2 with impurities, unstabilization of elemental properties and a deterioration in the dielectric voltage resistance are eliminated and further no operation of removing an oxide film and washing in the subsequent step are required. Also, since an organic coated and hardened film like the peeled and removed photoresist coated film exists as a solid in a process solution, its recovery is easy and hence waste water treatment is greatly simplified.

Brief Description of the Drawings

FIG. 1 and FIG. 2 are graphs showing the total solubility of liquefied carbon dioxide gas in an aqueous ethyl alcohol solution.

Agent Tatsuyuki UNUMA, patent attorney

Continued from page 1

(72) Inventor: Joshiro SATO

c/o Hitachi, Ltd., Hitachi Factory,

3-1-1, Saiwai-cho, Hitachi-shi.

(72) Inventor: Hideyuki YAGI

c/o Hitachi, Ltd., Hitachi Factory,

3-1-1, Saiwai-cho, Hitachi-shi.

FIG.1

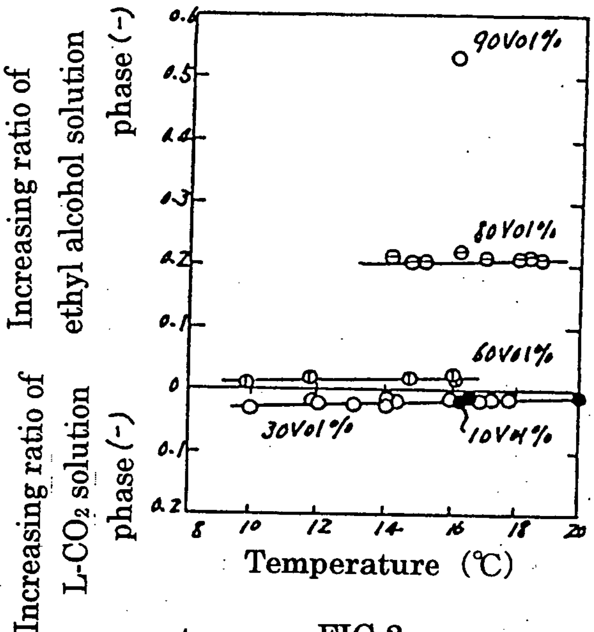
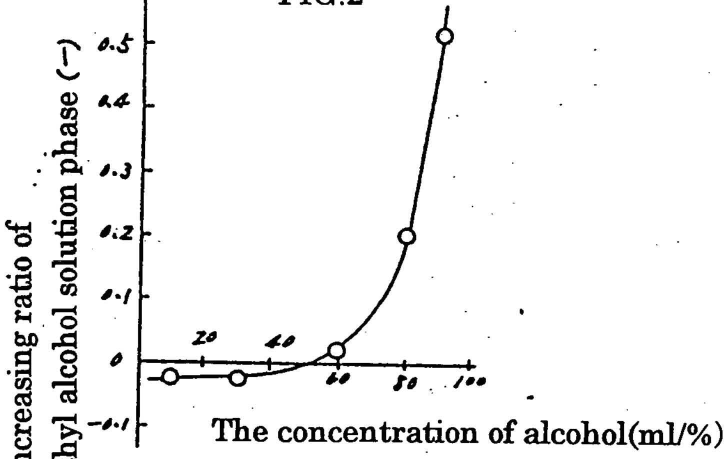

Increasing ratio of ethyl alcohol solution phase (−)
Increasing ratio of L-CO_2 solution phase (−)
90vol%
80vol%
60vol%
30vol%
10vol%
0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.2
8
10
12
14
16
18
20
Temperature (℃)

FIG.2


Increasing ratio of ethyl alcohol solution phase (−)
0.5
0.4
0.3
0.2
0.1
0
−0.1
20
40
60
80
100
The concentration of alcohol(ml/%)